

METHOD FOR PROTECTING PRODUCTS MADE OF A REFRACTORY MATERIAL AGAINST OXIDATION, AND RESULTING PROTECTED PRODUCTS

The present invention relates to protecting products made of refractory material against oxidation.

The term "refractory materials" is used herein to designate, in particular, refractory metals or metal alloys such as alloys based on niobium or based on molybdenum, tungsten, and/or tantalum, or refractory composite materials such as carbon-carbon composite materials or composite materials having a ceramic matrix, e.g. carbon-SiC (silicon carbide) composite materials. Such refractory materials are used, in particular, in the aviation or space industries to make parts that are subjected in operation to high temperatures, such as parts of aero-engines or elements of aerodynamic fairings (space vehicles).

A severe drawback common to the above-mentioned refractory materials is their poor resistance to oxidation, even when exposed to medium temperatures. This considerably limits the possibility of using them in an oxidizing medium at high temperature under static conditions, and makes such use practically impossible under aerodynamic conditions unless protection is provided against oxidation.

The state of the art concerning protecting refractory materials against oxidation is most abundant, in particular for composite materials containing carbon. The term "composite material containing carbon" is used herein to designate a composite material in which carbon is present in the reinforcing elements, e.g. in the form of carbon fibers, or in the matrix, or in an intermediate layer or "interphase" between the reinforcing elements and the matrix.

Generally, a protective coating is formed on the surface of the refractory material, the coating comprising a continuous layer of ceramic that withstands oxidation and that constitutes a barrier against the oxygen of the surrounding medium. The ceramic used may be a carbide, a nitride, a silicide, or an oxide. However, such a ceramic layer is inevitably subject to cracking. Microcracks appear in use because of the mechanical stresses imposed and/or the difference between the thermal expansion coefficients of the refractory material and of the protective coating. Similar defects may even appear while the ceramic layer is being made. The cracks provide the oxygen in the surrounding medium with direct access to the underlying refractory material.

To solve that problem, it is well known to make the coating so that it forms an outer surface layer that has healing properties, or to add such a layer to the ceramic layer. While the material is being used, variations in thermal and mechanical stresses give rise to variations in the shape of the cracks, particularly to their edges moving away from and towards each other. The term "healing layer" is used herein to designate a layer that is capable, under the conditions of use of the refractory material, of stopping, filling, or sealing the cracks while following the movements of the cracks, and capable of doing this without itself cracking. That is why the healing layer is usually made of substances that constitute a glass, or that are suitable for constituting a glass under the effect of oxidation, the glass being selected so as to exhibit viscous behavior at the working temperature of the material.

Thus, it is known that using a protective coating based on silicides provides protection against oxidation at high temperatures because a surface film is formed that is based on silica as a result of oxidizing the silicon contained in the

coating. In use, the silica-based film continuously re-constitutes itself, so long as a sufficient quantity of oxygen is supplied. The silica base has a healing function because it passes to the viscous state at high temperatures.

It has nevertheless appeared that in the presence of very high energy heat flows at high speed, e.g. in the combustion chamber of a direct air flow hypersonic jet engine, the silica film does not always regenerate quickly enough. The presence of intense heat flows that are localized, particularly in zones having surface defects, at sharp edges, and also in the zones of incidence of shockwaves, can give rise to rapid destruction of the surface oxide film and to combustion of the refractory material, which combustion can be self-sustaining when the oxidation reaction is highly exothermal.

In addition, a healing surface layer or film generally presents lower resistance to erosion than does the ceramic coating, and in the viscous state it runs the risk of being swept away. Unfortunately, in certain applications, in particular for parts of aero-engines or for fairing elements of space aircraft, the surface of the material is subjected to a gas flow that produces such a sweeping effect. This happens whether the healing surface layer is produced and regenerated by oxidizing components of the protective coating, or whether it is deposited in the form of an additional layer on the ceramic coating.

To overcome that difficulty, document EP-A-0 550 305 proposes making anti-oxidation protection by means of a healing phase and a refractory ceramic phase such as a carbide, a nitride, a silicide, or a boride, the phases constituting two inter-penetrating arrays. The protection is made on the surface of the product by depositing a mixture comprising: a refractory ceramic in finely divided form; at least one refractory oxide likewise in finely divided form and providing healing properties by forming a glass; and a binder constituted by a polymer that is a precursor for a refractory ceramic. By being cross-linked prior to transformation into a ceramic, the polymer makes it possible to establish a three-dimensional array that holds in place both the refractory ceramic component and the oxide component (s) of the healing phase. After the precursor polymer has been transformed into a ceramic, heat treatment performed at a temperature higher than the melting or softening temperature of the particles of the healing phase enables the healing phase fillers to bond together. This forms a continuous healing phase that is interpenetrated with the refractory ceramic phase, and that is thus made more suitable for withstanding abrasion and being swept away.

However, it is desirable, and this is the object of the invention, to further improve the performance of anti-oxidation protection to make it possible to use refractory materials at very high temperatures, typically with the material having a surface temperature of up to at least 1850° C., and also to guarantee that the healing function is continuous, even in surface zones which, because of their configuration or their location, are exposed to intense heat flows or to gas flows at very high speed.

According to the invention, this object is achieved by a coating for protection against oxidation that comprises a refractory phase that presents a branching microstructure forming an armature within which a healing phase is distributed,

the armature-forming refractory phase is mainly formed of the mixed refractory disilicide $Ti_{(0.4-0.95)}Mo_{(0.6-0.05)}Si_2$; and

the healing phase is constituted by a eutectic which is formed mainly of unbound silicon, of the mixed disilicide $Ti_{(0.4-0.95)}Mo_{(0.6-0.05)}Si_2$ and of at least the disilicide $TiSi_2$.